A value of 0.3 is assumed for χ_{mp} and χ_{sp}, α-methylstyrene and THF being considered as "good solvents" for the polymer.

From Figure 1, the variation of ϕ_m with ϕ_p is expressed by $\phi_m = 0.279 - 0.299\phi_p$. With $\phi_p = 0.1$, ϕ_m is equal to 0.249 and $\phi_s' = \phi_s/(\phi_s + \phi_m) = 0.725$. The corresponding value of -0.90 for χ_{ms} is deduced from Figure 2. Then

$$\beta = \chi_{ms} - \chi_{sp}(V_m/V_s) = -0.90 - 0.3 \times 1.60 = -1.38$$

Entering these values in eq 2, a value of 1.34 is obtained for $-(\Delta G_{1c}/RT)$.

$-(\Delta G_{1c}/RT)$, β and χ_{mp} being known, eq 8 is solved for a and yields $a = 0.282$. Finally, B is obtained from eq 7.

The Correlated Chain. A Statistical Model for Macromolecules[1]

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ABSTRACT: A new model chain for macromolecules is constructed by employing standard Fourier transform techniques. It is shown that the links of the model chain are directionally correlated; a measure of the correlation is expressed in terms of a chain flexibility parameter C_F. When $C_F = 1$, the model chain behaves like an uncorrelated random flight chain; as $C_F \rightarrow 0$ correlation increases until the model reduces to a rigid or rodlike chain. The intramolecular light scattering function $P(\mu)$ is evaluated for the model chain; $P(\mu)$ reduces to the usual expressions for flexible and rodlike chains for the limiting values of C_F.

I. Introduction

A problem of interest in macromolecular science is the characterization of the statistical properties of a real macromolecular chain; macromolecular solution properties (light scattering, intrinsic viscosity, etc.) are sensitive to the kind of configurational statistics obeyed by the chain.

A model chain that has been successful in interpreting the solution properties of flexible macromolecules in ideal (Θ) solvents is a random flight chain where the link vectors have identical, spherically symmetric, Gaussian distributions. However, this model and simple modifications of this model have enjoyed less success in describing the solution properties of flexible macromolecules in good solvents and for some nonflexible or "stiff" macromolecules in any solvent.

By employing Fourier transform techniques (Markoff's method[2]), a new statistical model for macromolecules is formulated in the present paper. The model is characterized by only two parameters: the mean square radius of gyration $\langle S^2 \rangle$ and the chain flexibility C_F, or equivalently, $\langle S^2 \rangle$ and the persistence length α. The model behaves like an uncorrelated random flight chain in one limit ($C_F = 1$) and like a rigid or rodlike chain in the other limit ($C_F = 0$) of chain flexibility. If a model is capable of describing both extremes of random flight chain behavior, then it may also be useful in simulating the statistical behavior of chains with intermediate statistical characteristics—the so-called "non-Gaussian" chains. The present model is an instructive alternative to several such models that have recently been proposed.[3-7]

II. Definition of the Model Chain

The reader is forewarned that the model to be described is not an attempt to describe explicitly the statistical behavior of a real macromolecular chain with fixed bond angles, hindered rotation, etc. Instead, an ideal chain will be defined that possesses the same general statistical character of a real chain, *viz.*, a chain which exhibits correlation of its bond vectors.

Consider a three-dimensional random flight chain composed of N statistically independent link vectors $(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ each having the same length b. Each vector makes an angle θ with the z axis; θ is always less than or equal to some arbitrary ϵ where $0 \leq \epsilon \leq \pi$. No restrictions are imposed on the remaining angle variable ϕ. The appropriate distribution function $\tau_j(\mathbf{r}_j)$ for random link vector $\mathbf{r}_j$ is

$$\tau_j(\mathbf{r}_j) = C\delta(|\mathbf{r}_j| - \mathbf{b}|)H(\epsilon - \theta) \qquad (1)$$

where (1) $\mathbf{b}$ is an arbitrary vector of fixed length, $|\mathbf{b}| \equiv b$; (2) $H(\epsilon - \theta)$ is a unit step function defined by

$$H(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \qquad (2)$$

(1) Taken in part from the Ph.D. Thesis of Isaac C. Sanchez, University of Delaware, 1969.

(2) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943); also in "Selected Papers on Noise and Stochastic Processes," N. Wax, Ed., Dover Publications, New York, N. Y., 1954.

(3) (a) Y. Tagami, *Macromolecules*, **2**, 8 (1969); (b) P. A. Sharp and V. A. Bloomfield, *J. Chem. Phys.*, **49**, 4564 (1968).

(4) D. McIntyre, J. Mazur, and A. M. Wims, *ibid.*, **49**, 2887 (1968).

(5) J. E. Hearst and R. A. Harris, *ibid.*, **46**, 398 (1967).

(6) G. Ver Strate and C. von Frankenberg, *J. Polym. Sci., Part A-2*, **5**, 1313 (1967).

(7) A. Peterlin, "Electromagnetic Scattering," H. Kerker, Ed., The Macmillan Co., New York, N. Y., 1963, pp 357–375, and references therein.

(3) $\delta(|\mathbf{r}_j| - |\mathbf{b}|) \equiv \delta(r_j - b)$ is a δ function; (4) C is a normalization constant which can be evaluated in spherical coordinates

$$\frac{1}{C} = \int_0^{2\pi} d\phi \int_0^{\infty} \delta(r_j - b) r_j^2 \, dr_j \int_0^{\pi} H(\epsilon - \theta) \sin\theta \, d\theta = 4\pi b^2 \sin^2(\epsilon/2) \quad (3)$$

The distribution function $\tau_j(\mathbf{r}_j)$ has been devised so that the domain of the random vector $\mathbf{r}_j$ can be restricted; if the domains of the N random vectors can be controlled by a single parameter ϵ, then the distribution of the sum of these random vectors will also be sensitive to the same parameter.

If a given configuration of the N link vectors is denoted by

$$[\mathbf{r}] \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \quad (4)$$

then the probability of that configuration

$$\tau[\mathbf{r}] \, d[\mathbf{r}] \equiv \tau(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N \quad (5)$$

is given by

$$\tau[\mathbf{r}] \, d[\mathbf{r}] \equiv \prod_{j=1}^{N} \tau_j(\mathbf{r}_j) \, d\mathbf{r}_j \quad (6)$$

III. Characteristic Functions

The end-to-end vector $\mathbf{R}$ is defined as

$$\mathbf{R} \equiv \sum_{j=1}^{N} \mathbf{r}_j \quad (7)$$

The distribution function $P(\mathbf{R})$ is obtained by integrating $\tau[\mathbf{r}]$ over all regions of $[\mathbf{r}]$ space in which eq 7 is satisfied. The integrations are carried out by introducing a three-dimensional Dirac δ function

$$P(\mathbf{R}) = \int \delta(\mathbf{R} - \sum_{j=1}^{N} \mathbf{r}_j) \tau[\mathbf{r}] \, d[\mathbf{r}] \quad (8)$$

where

$$\delta(\mathbf{x}) = (2\pi)^{-3} \int_{-\infty}^{\infty} \int \int \exp(i\mathbf{x}\cdot\mathbf{k}) \, d\mathbf{k} \quad (9)$$

Thus

$$P(\mathbf{R}) = (2\pi)^{-3} \int_{-\infty}^{\infty} \int \int \exp(-i\mathbf{R}\cdot\mathbf{k}) Q(\mathbf{k}) \, d\mathbf{k} \quad (10)$$

where $Q(\mathbf{k})$, the characteristic function[2] of the distribution, is given by

$$Q(\mathbf{k}) = \prod_{j=1}^{N} \int_{-\infty}^{\infty} \int \int \tau_j(\mathbf{r}_j) \exp(i\mathbf{k}\cdot\mathbf{r}_j) \, d\mathbf{r}_j = \prod_{j=1}^{N} q_j(\mathbf{k}) \quad (11)$$

The functions $q_j(\mathbf{k})$ are the characteristic functions associated with the link vectors $\mathbf{r}_j$; since all of the $\mathbf{r}_j$ are identically distributed (see eq 1), all of the $q_j(\mathbf{k})$ are identical and the subscript may be dropped. Therefore

$$q(\mathbf{k}) = \frac{\int_{\infty}^{\infty} \int \int \exp(i\mathbf{k}\cdot\mathbf{r}) \delta(r - b) H(\epsilon - \theta) \, d\mathbf{r}}{4\pi b^2 \sin^2(\epsilon/2)} \quad (12a)$$

Taking $\mathbf{k}$ parallel to the z axis, the integrations are carried out in spherical coordinates with the result

$$q(\mathbf{k}) = \frac{\exp(ibk) - \exp(ibk\cos\epsilon)}{2ibk \sin^2(\epsilon/2)} \quad (12b)$$

where $k \equiv |\mathbf{k}|$ and $r \equiv |\mathbf{r}|$. Substituting eq 12b into eq 11 and letting $f = \cos^2(\epsilon/2)$ leads to

$$Q(\mathbf{k}) = \exp(iNbkf) \left\{ \frac{\sin[(1-f)bk]}{[(1-f)bk]} \right\}^N \quad (13)$$

for limiting values of f, one finds

$$\lim_{f \to 0} (Q(\mathbf{k}) = \left[\frac{\sin(bk)}{bk} \right]^N \quad (14)$$

which is the characteristic function associated with an uncorrelated random flight chain of N vectors of identical length[2] and

$$\lim_{f \to 1} Q(\mathbf{k}) = \exp(iNbk) \quad (15)$$

which is the characteristic function of a rigid chain of length Nb. In the interesting case of large N

$$\lim_{N \to \infty} Q(k) = \exp\left\{ iNbkf - \frac{Nb^2(1-f)^2k^2}{6} \right\} \quad (16)$$

IV. Distribution Functions

The distribution function $P(\mathbf{R})$ of the end-to-end vector $\mathbf{R}$ in the limit of large N according to eq 10 and 16 is

$$P(\mathbf{R}) = (2\pi)^{-3} \int_{-\infty}^{\infty} \int \int \exp[-\gamma|\mathbf{k}|^2 + i(|\boldsymbol{\alpha}||\mathbf{k}| - \mathbf{k}\cdot\mathbf{R})] \, d\mathbf{k} \quad (17)$$

where

$$\gamma = Nb^2(1-f)^2/6 \quad (18)$$

$$|\boldsymbol{\alpha}| \equiv \alpha \equiv Nbf \quad (19)$$

The required integrations in eq 17 can be carried out in rectangular coordinates if the vector $\boldsymbol{\alpha}$ is collinear with $\mathbf{k}$, since $|\boldsymbol{\alpha}||\mathbf{k}| = \boldsymbol{\alpha}\cdot\mathbf{k}$; the required collinearity can always be achieved because the direction of the vector $\mathbf{b}$ (and hence $\boldsymbol{\alpha}$) is arbitrary. The integrals to be evaluated are then standard Fourier transforms and can be evaluated by contour integration to yield

$$P(\mathbf{R}) = (4\pi\gamma)^{-3/2} \exp\left[-\frac{|\mathbf{R} - \boldsymbol{\alpha}|^2}{4\gamma} \right] \quad (20)$$

Without loss of generality, one may require that $\boldsymbol{\alpha}$ be parallel to the z axis which implies that $\alpha_z = |\boldsymbol{\alpha}| = Nbf$ and $\alpha_x = \alpha_y = 0$. Equation 20 then becomes

$$P(\mathbf{R}) = (4\pi\gamma)^{-3/2} \exp\left[-\frac{R_x^2 + R_y^2 + (R_z - \alpha)^2}{4\gamma} \right] \quad (21)$$

Note that $P(\mathbf{R})$ is not spherically symmetric for $\alpha \neq 0$; the distribution is angle dependent.

To obtain the distribution function $P(R)$ for the end-to-end distance $|\mathbf{R}|$ independent of direction, a transformation is made to spherical coordinates where integration over the angle variables is performed

$$P(R) = R^2\int_0^{2\pi} d\phi \int_0^{\pi} P[\mathbf{R}(R,\theta,\phi)] \sin\theta \, d\theta = \frac{R}{\alpha(4\pi\gamma)^{1/2}}\left\{\exp\left[-\frac{(R-\alpha)^2}{4\gamma}\right] - \exp\left[-\frac{(R+\alpha)^2}{4\gamma}\right]\right\} \quad (22a)$$

or

$$P(R) = \frac{R}{\alpha(\pi\gamma)^{1/2}} \exp\left(-\frac{R^2+\alpha^2}{4\gamma}\right) \sinh\left(\frac{\alpha R}{2\gamma}\right) \quad (22b)$$

By considering the statistical behavior of a small portion of a large statistical chain, Ver Strate and von Frankenberg[6] obtained a distribution function with the same functional form as eq 22b; however, the parameter f in the present formulation is disposed differently. This improves the behavior in the rodlike limit.

Equation 20 indicates that each component of the vector $\mathbf{R}$ has a Gaussian distribution—a result that is not surprising. According to the central limit theorem of probability theory,[8] almost any choice of $\tau(\mathbf{r})$ should, as $N \to \infty$, result in a Gaussian distribution.

The distribution functions (21) and (22) have the desired properties of converging to the usual expressions for spherically symmetric, random flight chains ($N \to \infty$) as $f \to 0$ and of converging to δ functions as $f \to 1$. For example, eq 22 becomes

$$\lim_{f\to 0} P(R) = 4\pi R^2\left(\frac{3}{2\pi Nb^2}\right) \exp\left(-\frac{3R^2}{2Nb^2}\right) \quad (23)$$

It is well known that a δ function can be represented as

$$\delta(x-m) = \lim_{\sigma\to 0} (2\pi\sigma^2)^{-1/2} \exp\left[-\frac{(x-m)^2}{2\sigma^2}\right] \quad (24)$$

Therefore as $f \to 1$ eq 21 becomes

$$\lim_{f\to 1} P(\mathbf{R}) = \delta(R_x)\delta(R_y)\delta(R_z - Nb) \quad (25)$$

The next section will examine the properties of $P(R)$; the unique δ function character of $P(R)$ as $f \to 1$ will manifest itself.

V. Characterization of $P(R)$

The even moments $\langle R^{2k}\rangle$ of the distribution are defined as

$$\langle R^{2k}\rangle \equiv \int_0^{\infty} R^{2k} P(R)\, dR \quad (26)$$

The integration yields

$$\langle R^{2k}\rangle = (2k+1)!\gamma^k \sum_{n=0}^{k} \frac{(\alpha^2/\gamma)^n}{(2n+1)!(k-n)!} \quad (27)$$

For limiting values of f, one finds

$$\lim_{f\to 0} \langle R^{2k}\rangle = \frac{(2k+1)!}{k!}\left(\frac{Nb^2}{6}\right)^k \quad (28)$$

$$\lim_{f\to 1} \langle R^{2k}\rangle = (Nb)^{2k} \quad (29)$$

which are the even moments of a spherically symmetric, three-dimensional, Gaussian distribution and of a rigid chain of length Nb, respectively. As $f \to 0$ the even moments tend to be Gaussian (since $N \to \infty$) with the understanding that $\langle R^2\rangle = Nb^2$. In general, the distribution function for a random flight chain with short-range correlation will also be Gaussian[9,10] as $N \to \infty$, but then $\langle R^2\rangle$ is only proportional to Nb^2. The long-ranged correlated character of the present model (a property to be discussed in greater detail in section VII) destroys the linear relationship between $\langle R^2\rangle$ and Nb^2

$$\langle R^2\rangle = 6\gamma + \alpha^2 = Nb^2[(1-f)^2 + Nf^2] \quad (30)$$

Values for the most probable end-to-end distance R_{mp} are obtained by differentiating $P(R)$ with respect to R and equating the result to zero. This procedure yields the equation

$$\tanh\left(\frac{\alpha R_{mp}}{2\gamma}\right) = \frac{\alpha R_{mp}}{R_{mp}^2 - 2\gamma} \quad (31)$$

It can be easily verified that

$$\text{as } f \to 0,\ R_{mp}^2 = \frac{2Nb^2}{3} \quad \text{(Gaussian value)} \quad (32)$$

$$\text{as } f \to 1,\ R_{mp} = Nb \quad \text{(rod value)} \quad (33)$$

The values of $\langle R^{2k}\rangle$ and R_{mp} as $f \to 1$ show that eq 22 converges to a δ function in this limit.

VI. Distributions with Respect to the Center of Mass

The distribution function $P_j(\mathbf{S}_j)$ of $\mathbf{S}_j$, the random vector from the center of mass to the jth mass, is well known for a spherically symmetric, random flight chain ($N \to \infty$).[11,12] This distribution function can also be determined using the present model.

It will be assumed that each random link vector r_n is distributed according to eq 21, *i.e.*

$$\tau(\mathbf{r}) = \left[\frac{3}{2\pi b^2(1-f)^2}\right]^{3/2} \times \exp\left\{-\frac{3[r_x^2 + r_y^2 + (r_z - bf)]^2}{2b^2(1-f)^2}\right\} \quad (34)$$

For a chain of $N+1$ equal masses, a simple relation exists between link vectors and center of mass vectors

$$\mathbf{S}_j = \sum_{n=1}^{N}\left[\frac{n}{N+1} - H(n-j)\right]\mathbf{r}_n \quad (35)$$

where $H(n-j)$ is a unit step function defined by (2). It can be verified that eq 35 satisfies the condition

$$\sum_{j=0}^{N} \mathbf{S}_j \equiv 0 \quad (36)$$

(8) H. Cramer, "Mathematical Methods of Statistics," Princeton University Press, Princeton, N. J., 1963, pp 212–213.

(9) C. M. Tchen, *J. Chem. Phys.*, 214 (1952).
(10) B. H. Zimm, *J. Polym. Sci.*, 245 (1955).
(11) A. Isihara, *J. Phys. Soc. Jap.*, **5**, 201 (1950).
(12) P. Debye and F. Bueche, *J. Chem. Phys.*, **20**, 1337 (1952).

Since each component of $\mathbf{r}_n$ has a Gaussian distribution according to eq 34, the distribution of $\mathbf{S}_j$ can easily be determined from eq 35 by employing the addition theorem for Gaussian variables,[8] thus

$$P_j(\mathbf{S}_j) = \left[\frac{3}{2\pi(1-f)^2\sigma_j^2}\right]^{3/2} \times \exp\left\{-\frac{3[S_{xj}^2 + S_{yj}^2 + (S_{zj} - \bar{m}_j)^2]}{2(1-f)^2\sigma_j^2}\right\} \quad (37)$$

where

$$\bar{m}_j = \langle S_{zj}\rangle = \sum_{n=1}^{N}\left[\frac{n}{N+1} - H(n-j)\right]\langle r_z\rangle = Nbf[j/N - 1/2] \quad (38)$$

and

$$\sigma_j^2 = \langle S_j^2\rangle_{f=0} = b^2\sum_{n=1}^{N}\left[\frac{n}{N+1} - H(n-j)\right]^2 = Nb^2[(j/N - 1/2)^2 + 1/12] \quad (39)$$

where $N \gg 1$. For limiting values of f, eq 37 becomes

$$\lim_{f\to 0} P_j(\mathbf{S}_j) = \left(\frac{3}{2\pi\sigma_j^2}\right)^{3/2}\exp\left\{-\frac{3S_j^2}{2\sigma_j^2}\right\} \quad (40)$$

which is the usual expression for a random flight chain as $N \to \infty$ and

$$\lim_{f\to 1} P_j(S_j) = \delta(S_{xj})\delta(S_{yj})\delta[S_{zj} - Nbm_j] \quad (41)$$

which is an appropriate expression for a rigid chain where $m_j = j/N - 1/2$.

By inspection of (37), one finds

$$\langle S_j^2\rangle = (1-f)^2\sigma_j^2 + \alpha^2 m_j^2 \quad (42)$$

The mean-square radius of gyration $\langle S^2\rangle$ is defined by

$$\langle S^2\rangle = (N+1)^{-1}\sum_{j=0}^{N}\langle S_j^2\rangle \quad (43)$$

For large N

$$\langle S^2\rangle = \frac{Nb^2}{6}\left[(1-f)^2 + \frac{Nf^2}{2}\right] = \gamma + \frac{\alpha^2}{12} \quad (44a)$$

$$\langle S^2\rangle_{f=0} = \frac{Nb^2}{6} \quad \text{(flexible chain value)} \quad (44b)$$

$$\langle S^2\rangle_{f=1} = \frac{(Nb)^2}{12} \quad \text{(rod value)} \quad (44c)$$

It can be verified that the above result for $\langle S^2\rangle$ is obtained when $\langle S^2\rangle$ is given as (Lagrange formula[13])

$$\langle S^2\rangle = (N+1)^{-2}\sum_{i<j}\sum\langle R_{ij}^2\rangle \quad (45)$$

and it is assumed that R_{ij}, the distance between the ith and jth mass, is distributed in the same way as the end-to-end distance R.

VI. Light Scattering

The intramolecular interference scattering function $P(\mu)$ (often denoted as $P(\theta)$) appropriate for a macromolecule with $N+1$ scattering centers is[14]

$$P(\mu) = (N+1)^{-2}\sum_{k=0}^{N}\sum_{l=0}^{N}\left\langle\frac{\sin(\mu R_{kl})}{(\mu R_{kl})}\right\rangle \quad (46)$$

where $R_{kl} = |\mathbf{R}_l - \mathbf{R}_k|$ and $\mu = (4\pi/\lambda)\sin(\theta/2)$ with λ the wavelength of the light in the scattering medium and θ the scattering angle.

If we assume that the intersegment distances R_{kl} obey the same kind of statistics as the end-to-end distance, or equivalently, if the link vectors are distributed according to eq 34, then the distance distribution function $P(R_{kl})$ has the same functional form as $P(R)$ given by eq 22. Therefore

$$\left\langle\frac{\sin(\mu R_{kl})}{\mu R_{kl}}\right\rangle = \int_0^\infty P(R_{kl})\frac{\sin(\mu R_{kl})}{\mu R_{kl}}\,dR_{kl} = \frac{\sin(\mu bf|l-k|)}{(\mu bf|l-k|)}\exp[-\mu^2 b^2(1-f)^2|l-k|/6] \quad (47)$$

Substituting eq 47 into eq 46 and converting sums to integrals ($N \gg 1$), one obtains

$$P(\mu) = \frac{2}{N^2}\int_0^N (N-x)\frac{\sin(\mu bfx)}{(\mu bfx)} \times \exp[-\mu^2 b^2(1-f)^2 x/6]\,dx \quad (48)$$

which becomes after a simple change of variable

$$P(\mu) = 2\left\{\int_0^1\frac{\sin(ay)}{ay}\exp(-cy)\,dy + \frac{\exp(-c)(c\sin a + a\cos a - a)}{a(a^2+c^2)}\right\} \quad (49)$$

where

$$a \equiv \alpha\mu \equiv (Nbf)\mu \quad (50)$$

$$c \equiv \gamma\mu^2 \equiv \frac{Nb^2(1-f)^2}{6}\mu^2 \quad (51)$$

The remaining integral in (49) cannot be expressed in terms of any of the usual transcendental functions; however, it can be easily evaluated by standard numerical integration procedures (Simpson's rule, etc.) or by other numerical procedures.[15]

It can be verified that

$$\lim_{\mu\to 0} P(\mu) = 1 - \frac{\langle S^2\rangle}{3}\mu^2 + \cdots \quad (52)$$

as it should where $\langle S^2\rangle$ is given by eq 44a.

Furthermore, for limiting values of f one finds

$$\lim_{f\to 0} P(\mu) = (2/x^2)[\exp(-x) - 1 + x] \quad (53)$$

and

$$\lim_{f\to 1} P(\mu) = \frac{2}{\mu L}\int_0^{\mu L}\frac{\sin y}{y}\,dy - \left[\frac{\sin(\mu L/2)}{(\mu L/2)}\right]^2 \quad (54)$$

where L is the extended length of the chain ($L = Nb$) and

$$x = \mu^2\langle S^2\rangle_{f=0} = \mu^2(Nb^2/6) \quad (55)$$

Equations 53 and 54 are the well-known expressions for a Gaussian chain (all intersegment distances have spherically symmetric, Gaussian distributions) and a rigid chain of length L, respectively.

(13) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969, p 383.
(14) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).
(15) I. C. Sanchez, Ph.D. Thesis, University of Delaware, 1969, Appendix H.

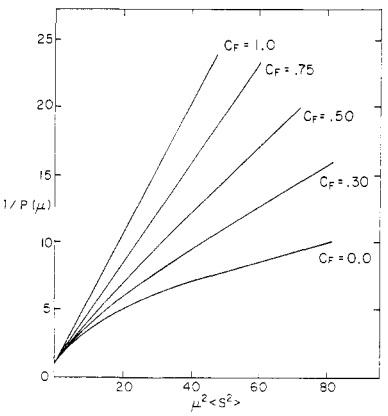

Figure 1. The reciprocal light scattering function for the correlated chain. The scattering curves for $C_F = 1$ and $C_F = 0$ are appropriate for a Gaussian coil and a rigid rod, respectively.

To facilitate the investigation of the behavior of $P(\mu)$ for intermediate values of f, it is convenient to define a chain flexibility parameter C_F $(0 \leq C_F \leq 1)$

$$C_F \equiv \frac{c}{c + a^2/12} \equiv (1 - f)^2 \frac{\langle S^2 \rangle_{f=0}}{\langle S^2 \rangle} \tag{56}$$

and if $v = \mu^2 \langle S^2 \rangle$, then

$$c = vC_F \tag{57}$$

$$a^2 = 12v(1 - C_F) \tag{58}$$

By definition C_F is proportional to the ratio of the mean square gyration radii of the uncorrelated chain to the correlated chain. Note also that $f = \alpha/L$ where L is the extended length of the chain Nb. In the next section α will be identified as the persistence length of the chain.

In Figure 1 the reciprocal scattering function $1/P(\mu)$ has been plotted against v for several values of C_F. When $C_F = 1$, $P(\mu)$ reduces to eq 53 and when $C_f = 0$, $P(\mu)$ reduces to eq 54.

VII. Discussion

Real macromolecular chains exhibit an important statistical property: the bond or link vectors are not *directionally* independent of one another. The link vectors are correlated. This statistical feature peculiar to real macromolecular chains is also characteristic of the present model.

A necessary but not sufficient condition for directional independence is that

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = 0 \qquad i \neq j \tag{59}$$

If all projections of the jth link vector onto the ith link vector occur with equal probability, then it can be easily shown that eq 59 follows. A real macromolecular chain will never satisfy (59) for all pairs of i and j; however as $|i - j|$ becomes large condition 59 is more nearly obeyed, especially for macromolecules in Θ solvents.

The case where $\mathbf{r}_i$ and $\mathbf{r}_j$ are always perpendicular to one another $(\mathbf{r}_i \cdot \mathbf{r}_j = 0)$ serves to illustrate that eq 59 is not a sufficient condition for directional independence. On the other hand, when condition 59 is not satisfied it can be assumed that the link vectors are correlated.

When N is large, eq 34 is an adequate and convenient representation of the link vector distribution function for the new model chain. It can be readily verified (by inspection) that for *all pairs* of i and j $(i \neq j)$

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = (bj)^2 \tag{60}$$

i.e., the link vectors are directionally correlated. For a real macromolecular chain the quantity $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$, which for convenience will be referred to as the "correlation," will depend on $|i - j|$ as well as the relative positions of the links along the chain—a feature not characteristic of the present model. If the model is to be representative of the real chain, then eq 60 must be interpreted as an average correlation between the $N(N - 1)$ pairs of link vectors. The average correlation denoted by $\overline{\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle}$ for a real chain can be defined as

$$\overline{\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle} \equiv \frac{1}{N(N - 1)} \sum_{i \neq j}^{N} \sum^{N} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle \tag{61}$$

Only when $f = 0$ (or when $C_F = 1$) is the end-to-end vector distribution (21) spherically symmetric; correlation destroys the spherical symmetry around the origin and shifts it to the point $(0,0,Nbf)$. Concomitant with the shift in the center of symmetry is a decrease in the width of the distribution, *i.e.*, the variance of each component $(\sigma_x^2, \sigma_y^2, \sigma_z^2)$ decreases as $f \rightarrow 1$

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 2\gamma = \frac{Nb^2}{3}(1 - f)^2 \tag{62}$$

Correlation reduces the multiplicity of configurations available to the chain; moreover, the over-all effect is that correlation produces in the distribution a "persistence of direction," a tendency to extend more in one direction than in any other. Each link vector is systematically displaced in the z direction by bf units. Superimposed on this displacement is a random distribution symmetrically disposed around the point $(0,0,bf)$. The idea of a persistence length for the model chain arises quite naturally; the persistence length can be defined as the mean projection of the end-to-end vector in the direction of the first link of the chain. The direction of the first link establishes an axis of orientation for a chain with correlation. In the present theory, the z axis is the axis of orientation; the mean projection of the end-to-end vector on this axis is α or Nbf.

The persistence length α and the undefined parameter γ appearing in many of the previous equations can be expressed in terms of $\langle S^2 \rangle$, an experimentally measurable quantity, and the chain flexibility parameter C_F (*cf.* eq 57 and 58)

$$\gamma = C_F \langle S^2 \rangle \tag{63}$$

$$\alpha^2 = 12 \langle S^2 \rangle (1 - C_F) \tag{64}$$

It can also be easily verified that the mean square end-to-end distance $\langle R^2 \rangle$ is related to $\langle S^2 \rangle$ and C_F by

$$\langle R^2 \rangle = 6(2 - C_F) \langle S^2 \rangle \tag{65}$$

Furthermore, from eq 63 and 64, one finds

$$\gamma = \frac{C_F}{6(2 - C_F)}\langle R^2\rangle \quad (66)$$

$$\alpha^2 = \frac{2(1 - C_F)}{(2 - C_F)}\langle R^2\rangle \quad (67)$$

Using eq 66 and 67 the end-to-end distance distribution function (22) can be rewritten as

$$P(x)\mathrm{d}x = \frac{x}{\bar{\alpha}(4\pi\bar{\gamma})^{1/2}}\left\{\exp\left[-\frac{(x - \bar{\alpha})^2}{4\bar{\gamma}}\right] - \exp\left[-\frac{(x + \bar{\alpha})^2}{4\bar{\gamma}}\right]\right\}\mathrm{d}x \quad (68)$$

where $x = R/\langle R^2\rangle^{1/2}$ and $\bar{\gamma} \equiv \gamma/\langle R^2\rangle$ and $\bar{\alpha} = \alpha/\langle R^2\rangle^{1/2}$. Figure 2 illustrates the behavior of $P(x)$ for some values of C_F.

Aside from its use as a model for relatively stiff macromolecules, the correlated chain may be useful in describing the light scattering from flexible macromolecules in good solvents. Recently, Smith and Carpenter[16] published light-scattering data for relatively sharp fractions of polystyrene in good solvents. They found that one high molecular weight fraction (*ca.* five million) when dissolved in benzene at 30° deviates substantially from the ideal scattering equation (53); the deviation was attributed to excluded volume effects and not to the polydispersity of the sample. The data were explained by assuming that the distance R_{ij} between scattering centers i and j was distributed according to a Gaussian law but with a modified mean square distance, *i.e.*

$$\langle R_{ij}^2\rangle = b^2|i - j|^{1+\epsilon} \quad (69)$$

The scattering function for a chain obeying these modified Gaussian statistics is

$$P(\mu) = 2\int_0^1 (1 - x)\exp\left\{-c\left(1 + \frac{5\epsilon}{6} + \frac{\epsilon^2}{6}\right)x^{1+\epsilon}\right\}\mathrm{d}x \quad (70)$$

where $c = \mu^2\langle S^2\rangle$. A scattering curve for $\epsilon = 0.11$ (a value determined by trial and error) and the given experimental root mean square gyration radius $\langle S^2\rangle^{1/2}$ (1400Å) essentially reproduces the experimental scattering curve. The present model is also able to explain the data for the given gyration radius and a chain flexibility of $C_F = 0.65$ (best fit value). From eq 64 and 65, the persistence length α and the root mean square end-to-end distance $\langle R^2\rangle^{1/2}$ are

$$\alpha = 2800 \text{ Å}$$

$$\langle R^2\rangle^{1/2} = 4000 \text{ Å}$$

It is interesting to note that the value of $\langle R^2\rangle^{1/2}$ is about 16% higher than expected (4000 Å *vs.* 3400 Å) if it is assumed that

$$\langle R^2\rangle = 6\langle S^2\rangle \quad (71)$$

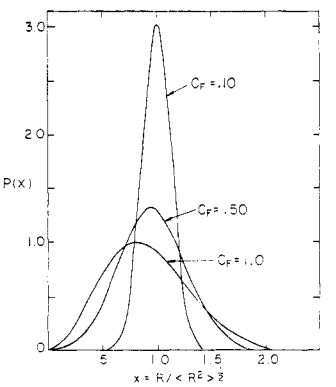

Figure 2. Behavior of the end-to-end distance distribution function (eq 68) near its root mean square value as a function of chain flexibility.

Equation 71 is the usual relationship between $\langle R^2\rangle$ and $\langle S^2\rangle$ as $N \to \infty$ for a random flight chain in the absence of excluded volume effects.

Kirste[17] has pointed out that although a one-to-one correspondence exists between the configurational statistics of the model chain and the scattering function, it has not been shown that a scattering function uniquely defines the statistical character of the chain. Several different models may be capable of interpreting an experimental scattering curve, especially in the usual experimentally accessible light scattering region. For this reason we have not undertaken the task of making a detailed comparison of the various model theories of light scattering.

From an experimental point of view, the utility of a given model can probably be ascertained best by examining more than just the light scattering properties of a given macromolecular solution. For example, if the parameters which enter a theory can be determined by light scattering, then these parameters may be used to predict other solution properties. Recently Bur and Roberts[18] interpreted the dipole moment data of poly(butyl isocyanate) in terms of the wormlike chain of Kratky and Porod.[7] Data of this kind combined with light scattering data can provide the basis for a better comparison of the various theories. From a theoretical point of view, the correlated chain is an attractive model because it recognizes (albeit incorrectly) the inherent correlated character of a real chain; it also behaves correctly in the limit of mimimum and maximum correlation. Moreover, it is a two parameter theory where one of the parameters, the mean square gyration radius, can be determined by light scattering without making any assumptions concerning the configurational statistics of the chain.

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